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㉘ Process for producing aromatic polycarboxylic acid with high purity.

㉙ An aromatic polycarboxylic acid with high purity is produced by oxidizing a polyalkyl-substituted aromatic aldehyde or polyalkyl-substituted aromatic carboxylic acid with molecular oxygen in water as a solvent in the presence of bromine ion or bromine ion and heavy metal ion as a catalyst, contacting the oxidation reaction product with molecular hydrogen in the presence of a hydrogenating catalyst at a temperature of 100° to 200°C, and then separating an aromatic polycarboxylic acid from the hydrogenated product.

PROCESS FOR PRODUCING AROMATIC POLYCARBOXYLIC ACID  
WITH HIGH PURITY

1           The present invention relates to a process for  
producing an aromatic polycarboxylic acid with high  
purity by oxidizing a polyalkyl-substituted aromatic  
aldehyde or a polyalkyl-substituted aromatic carboxylic  
5 acid in water as a solvent in the presence of a bromine  
ion-containing catalyst.

Among aromatic polycarboxylic acids, tri-  
mellitic acid is widely used as raw materials for alkyd  
resin, high grade plasticizer, polyamide-imide poly-  
10 ester, and pyromellitic acid is used as raw materials  
for special plasticizer, polyimide and crosslinking  
agent.

However generally high purity is required for  
the aromatic polycarboxylic acids for such uses. For  
15 example, trimellitic acid must have a purity of higher  
than 99 %, and a TEG color test value of less than 170  
(TEG color test value designates a coloring degree where  
a smaller TEG value means less content of coloring  
matters).

20           The so far well known processes for producing  
trimellitic acid in a commercial scale include (i) a  
process by oxidizing pseudocumene as a raw material with  
air at 1 to 3 stages in acetic acid as a solvent in the  
presence of a Co-Mn-Br catalyst and (ii) a process by  
25 oxidizing pseudocumene as a raw material with nitric

- 1 acid likewise. Recently, (iii) a process by oxidizing dimethylbenzaldehyde with air in water as a solvent in the presence of bromine and a metal catalyst [Japanese Patent Application Kokai (Laid-open) No. 26839/81].
- 5 These three processes (i) - (iii) require different raw materials, solvents, catalysts and oxidizing agents, and thus produce quite different impurities as by-products, though the same trimellitic acid is the desired product.

In the process (i), the main impurities are

10 tetra or pentacarboxylic acid of condensed two nuclei and tarry high molecular weight substances. In the process (ii), they are nitro compounds originating from the nitric acid as the oxidizing agent. In the process (iii), on the other hand bromine compounds are produced

15 as impurities. Thus, different purification means are required for the production of trimellitic acid with high purity, depending upon the individual processes.

As a result of extensive studies of a commercially advantageous process for purifying crude tri-

20 mellitic acid from the process (iii), the present inventors found that impurities could be very simply removed by hydrogenating the reaction product in the presence of a noble metal of Group 8 of the periodic table, for example, palladium, as a hydrogenating catalyst, whereby

25 trimellitic acid with high purity could be obtained.

On the other hand, a somewhat similar process for purification is disclosed (Japanese Patent

1 Publication No. 16860/66), where fiber grade terephthalic acid is produced by treating an impure aqueous terephthalic acid solution containing a large amount of 4-carboxybenzaldehyde and coloring impurities, as  
5 obtained by catalytic liquid phase oxidation of para-xylene with molecular oxygen, with a reducing agent in the most preferable temperature range of 225° to 275°C. However, the desired effect of purification cannot be obtained by applying the process as such to the treat-  
10 ment of the bromine compounds produced as by-products in the process (iii), for most of trimellitic acid rather than the bromine compounds is further converted to methylphthalic acid, phthalic acid and even to toluic acid under the said hydrogenating conditions, which lead  
15 to considerable deterioration of distillation efficiency and product purity.

As a result of further studies of reaction selectivity in hydrogenation of trimellitic acid and bromine compounds, the present inventors have found  
20 that, by conducting hydrogenation at a hydrogenation temperature of 100° to 200°C the bromine compounds can be removed while preventing hydrogenating of trimellitic acid, and have established the present invention.

## 25 SUMMARY OF THE INVENTION

The present invention provides a process for producing an aromatic polycarboxylic acid with high

1 purity, which comprises oxidizing a polyalkyl-  
substituted aromatic aldehyde or polyalkyl-substituted  
aromatic carboxylic acid with molecular oxygen in water  
as a solvent in the presence of bromine ion or bromine  
5 ion and heavy metal ion as a catalyst, contacting the  
oxidation reaction product with molecular hydrogen in  
the presence of a hydrogenating catalyst at a tempera-  
ture of 100° to 200°C, and then separating an aromatic  
polycarboxylic acid from the hydrogenated product.

10 The polyalkyl-substituted aromatic aldehyde to  
be used as the raw material in the oxidation reaction  
according to the present invention includes 2,4-  
dimethylbenzaldehyde, 3,4-dimethylbenzaldehyde, 2,4,5-  
trimethylbenzaldehyde, 2,4,6-trimethylbenzaldehyde,  
15 etc., which are correspondingly oxidized to trimellitic  
acid, pyromellitic acid, mellophannic acid, etc.

The polyalkyl-substituted aromatic aldehyde  
can be stoichiometrically synthesized without any pro-  
duction of isomers as by-product by reacting a polyalkyl  
20 benzene with carbon monoxide in the presence of a cata-  
lyst of HF-BF<sub>3</sub> system.

In the present invention, polyalkyl-substi-  
tuted aromatic carboxylic acid can be likewise used as  
a raw material for the oxidation reaction. Examples of  
25 the polyalkyl-substituted carboxylic acid include  
2,4-dimethylbenzoic acid, 3,4-dimethylbenzoic acid,  
2,4,5-trimethylbenzoic acid, 2,4,6-trimethylbenzoic

1 acid, etc., which are correspondingly oxidized to tri-  
mellitic acid, pyromellitic acid, mellophannic acid,  
etc.

5 Bromine ion can be used as the catalyst in the  
oxidation reaction, but it is preferable to use bromine  
ion together with heavy metal ion. Particularly pre-  
ferable heavy metal ion is manganese ion and cerium ion.  
Some heavy metals such as palladium, ruthenium, bismuth,  
niobium, thallium, tellurium, vanadium, etc. deteriorate  
10 the catalytic activity of bromine ions, and cannot be  
used as the catalyst. A bromine ion-liberating compound  
can be also used, so far as it can liberate bromine ions  
in the course of oxidation reaction. For example,  
hydrogen bromide, ammonium bromide, sodium bromide, or  
15 organobromo compounds such as alkyl bromide, etc. can be  
used.

The amount of bromine ions as the catalyst is  
0.5 to 12 % by weight, preferably 0.5 to 6 % by weight  
on the basis of water as the solvent. The amount of the  
20 heavy metal ion as the catalyst in the equivalent weight  
or less than the equivalent weight to that of the bro-  
mine ion. The amount of water as the solvent is not  
particularly limited, but preferably is at least equal  
to the weight of the aldehyde or the carboxylic acid as  
25 the raw material.

In the present invention, oxidation reaction  
temperature is 180° - 280°C, preferably 200° - 260°C.  
Oxydation reaction pressure is automatically set by

1 keeping the reaction temperature constant generally by  
evaporation and condensation and refluxing operation of  
water as the solvent, but it is also possible to keep  
the oxidation reaction pressure at a desired value by  
5 the external heat exchanger. Any pressure can be  
applied so far as it is within a pressure range in which  
the reaction solution can be kept in a liquid phase, and  
usually a pressure 15 - 60 kg/cm<sup>2</sup> gage is used.

The oxidation reaction can be carried out  
10 batchwise, semi-continuously, or continuously, but the  
best effect can be obtained particularly when the pre-  
sent invention is applied to the conventional continuous  
oxidation process requiring a plurality of reactors at  
a plurality of stages.

15 The reaction product from the oxidation reac-  
tion is subjected to cooling, crystallization and solid-  
liquid separation, and then the resulting crude aromatic  
polycarboxylic acid is dissolved in water, and then the  
aqueous solution is supplied to a hydrogenating reac-  
20 tor, or the reaction product as such is supplied to the  
hydrogenating reactor without any solid-liquid separa-  
tion. No such solid-liquid separation is required under  
such an oxidation condition to produce less by-products  
of bromine compounds as impurities. The crude aqueous  
25 polycarboxylic acid solution to be hydrogenated usually  
has a polycarboxylic acid concentration of 15 to 50 % by  
weight, and it is desirable to supply the crude aqueous

1 solution at a lower polycarboxylic acid concentration in  
the case of a higher content of bromine compounds in the  
case of a larger amount of bromine ions being used as  
the oxidation catalyst. The preferable concentration of  
5 bromine ion is 0.2 - 1.0% by weight in the hydrogenating  
reaction.

The hydrogenation catalyst includes catalysts  
containing at least one of noble metal species belonging  
to group 8 of the periodic table, for example, Pd, Pt,  
10 Ru, Rh, etc. These noble catalysts can be used in any  
form, for example, simple substance, alloy, mixture or  
carrier-supported catalyst, preferably an activated  
carbon-supported catalyst. The carrier may be in a  
powder form or in a pellet form, but the pellet form is  
15 often advantageous for continuous operation because of  
its applicability to a fixed bed.

Hydrogenation temperature is 100° - 200°C,  
preferably 100° - 180°C. Hydrogen pressure is high  
enough to keep the crude aqueous polycarboxylic acid  
20 solution in a liquid state, and is usually 5 - 30  
kg/cm<sup>2</sup> gage, preferably 5 - 20 kg/cm<sup>2</sup> gage.

Hydrogenation time depends upon the concentration of  
bromine compounds as impurities, hydrogenation tem-  
perature, the amount of catalyst, the catalyst activity  
25 and the desired purity of product polycarboxylic acid,  
and is usually 0.1 to 8 hours, preferably 0.2 to 3  
hours. The catalyst containing 0.5 % by weight of a



1 noble metal catalyst supported on a carrier on the basis  
of the carrier is used in an amount of 0.05 to 5.0 % by  
weight on the basis of polycarboxylic acid for batchwise  
hydrogenation under the said hydrogenation conditions.

5 The hydrogenation can be carried out batch-  
wise, semi-batchwise, or continuously. According to the  
conventional process, the hydrogenation product mixture  
is then subjected to dehydration by heating, and the  
resulting anhydrous mixture is then subjected to  
10 distillation under a subatmospheric pressure to obtain  
an anhydrous aromatic polycarboxylic acid product.

According to the present invention, an aroma-  
tic polycarboxylic acid with high purity can be readily  
obtained from the crude aromatic polycarboxylic acid  
15 obtained by oxidation of a polyalkyl-substituted aroma-  
tic aldehyde or polyalkyl-substituted aromatic carboxylic  
acid in the presence of bromine ion as a catalyst.

#### PREFERRED EMBODIMENTS OF THE INVENTION

20 The present invention will be described in  
detail below, referring to Examples, where the bromine  
content is a content of bromine compounds in terms of  
bromine determined by X-ray fluorometry analysis on the  
basis of trimellitic acid; TEG color is an APHA number  
25 index of the color of heated solution consisting of 4.0  
g of trimellitic anhydride and 30.0 g of triethylene  
glycol, where a smaller value of TEG color means less  
content of coloring matters; purity is a percentage of

1 the acid value of product trimellitic acid to the acid  
value of pure trimellitic acid; and distillation yield  
is a percentage of the amount of main fraction as a  
distillate, to the amount of it in a feedstock to the  
5 distillation.

#### Example 1

(Direct hydrogenation without solid-liquid separation)

Into an autoclave made from zirconium having  
10 a net capacity of 2 with a reflux condenser, a  
stirrer, a heater, a raw material inlet, a gas inlet,  
a gas outlet and a product outlet were charged 500 g of  
water, 15 g of manganese bromide tetrahydrate, and 7 g  
of hydrogen bromide. Nitrogen was introduced under  
15 pressure into the autoclave at the gas inlet to elevate  
the inside pressure of the autoclave to  $10 \text{ kg/cm}^2$  gage.  
The autoclave was heated to  $220^\circ\text{C}$  by a heater and then  
2,4-dimethylbenzaldehyde having a purity of at least  
99.5 % was introduced into the autoclave at a rate of  
20 4.17 g/min. At the same time, air was introduced into  
the autoclave at a controlled flow rate to keep the  
oxygen concentration of the effluent gas from the  
autoclave at 3 - 4 % by volume. 2,4-dimethylbenzalde-  
hyde was continuously introduced into the autoclave for  
25 60 minutes, while air was supplied, even after the  
introduction of 2,4-dimethylbenzaldehyde was finished,  
to the autoclave for further 20 minutes to complete oxi-  
dation. The oxidation product was cooled to  $20^\circ\text{C}$ , and

1 then taken out of the autoclave. The oxidation product  
had a bromine content of 6,500 ppm and had a purity of  
95.6 % by weight in terms of trimellitic acid.

5 970.5 g of the oxidation product containing  
356.5 g of trimellitic acid was charged into an auto-  
clave having a net capacity of 2 l, provided with a  
catalyst basket with 1 g of a 0.5 wt.% Pd-C catalyst,  
and then the autoclave was pressurized with a hydrogen  
gas under a pressure of 15 kg/cm<sup>2</sup> gage, and then heated  
10 at 150°C for 2 hours while injecting the hydrogen gas  
into the liquid phase and passing it through the auto-  
clave to conduct hydrogenation. Then, the autoclave was  
slowly cooled to 20°C, and the precipitated crystal was  
recovered by filtration and dried. The thus obtained  
15 trimellitic acid was placed into a distilling still and  
heated at 230°C to 240°C under a pressure of 50 to 100  
mmHg (absolute) to conduct dehydration, and then  
distilled at 230° to 240°C under a pressure of 4 to 5  
mmHg (absolute) to obtain trimellitic anhydride. The  
20 thus obtained trimellitic anhydride had a purity of  
99.5 %, a bromine content of 150 ppm, a TEG color value  
of 60 and a distillation yield of 97.5 %.

#### Comparative Example 1

25 The oxidation product as obtained in Example 1  
was slowly cooled to 20°C without hydrogenation, and 358  
g of the precipitated crude trimellitic acid crystal was

- 1 placed in a distilling still, and heated at 230° - 240°C under a pressure of 50 - 100 mmHg (absolute) to conduct dehydration and then distilled at 230° - 240°C under a pressure of 4 - 5 mmHg (absolute) to obtain
- 5 trimellitic anhydride. The resulting trimellitic anhydride had a purity of 96.5 %, a bromine content of 5,000 ppm, TEG color value of 800 and a distillation yield of 93.2 %.

10 Comparative Example 2

- The reaction product as obtained in Example 1 was slowly cooled to 20°C without hydrogenation, and 358 g of the precipitated crude trimellitic acid crystal was separated and admixed with 1,100 g of water. Then,
- 15 the mixture was heated to 100°C to dissolve the crude trimellitic acid crystal. Then, the solution was cooled to 20°C, and the precipitated crystal was recovered by filtration, and subjected to dehydration and distillation in the same manner as in Example 1 to obtain
- 20 trimellitic anhydride. The thus obtained trimellitic anhydride had a purity of 97.0 %, a bromine content of 4,500 ppm, a TEG color value of 750, and a distillation yield of 94.0 %.

25 Example 2

(Solid-liquid separation and hydrogenation)

The oxidation product as obtained in Example 1 was cooled slowly to 20°C, and 358 g of the precipitated

1 crystal was separated and admixed with 550 g of water.  
The resulting slurry was charged into an autoclave  
having a 2-l capacity, provided with a catalyst basket  
with 1 g of 0.5 % Pd/C catalyst. Then, the autoclave  
5 was pressurized with a hydrogen gas under a pressure of  
15 kg/cm<sup>2</sup> gage and then heated at 150°C for 1.5 hours,  
while passing the hydrogen gas through the autoclave to  
conduct hydrogenation. Then, the autoclave was slowly  
cooled to 20°C, and the precipitated crystal was reco-  
10 vered by filtration and dried. Then, the resulting  
trimellitic acid was placed in a distilling still and  
subjected to dehydration and distillation in the same  
manner as in Example 1 to obtain trimellitic anhydride.  
The resulting trimellitic anhydride had a purity of  
15 99.7 %, a bromine content of 70 ppm, a TEG color value  
of 40, and a distillation yield of 98.0 %.

### Comparative Example 3

When the crude trimellitic acid crystal was  
20 dissolved in Comparative Example 2, 20 g of activated  
carbon granules was added to the solution. The result-  
ing mixture was kept at 100°C with stirring for 60  
minutes and then filtered, while hot, to remove the  
activated carbon granules. The filtrate was slowly  
25 cooled to 20°C, and the precipitated crystal was  
recovered by filtration, and subjected to dehydration  
and distillation in the same manner as in Example 1 to

1 obtain trimellitic anhydride. The resulting trimellitic  
anhydride had a purity of 97.2 %, a bromine content of  
4,100 ppm, a TEG color value of 600, and a distillation  
yield of 94.2 %. It was found that the impurities  
5 could not removed by adsorption with the activated  
carbon.

### Example 3

(Solid-liquid separation and hydrogenation)

10 The oxidation product as obtained in Example  
1 was slowly cooled to 20°C to separate 358 g of precipitated  
crude crystal, and the crude crystal was admixed  
with 550 g of water in the same manner as in Example 2.

Then, the resulting slurry was charged into  
15 an autoclave having a 2-l capacity, provided with a  
catalyst basket with 0.5 g of 0.5 % Pd/C catalyst, and  
the autoclave was pressurized with a hydrogen gas under  
a pressure of 25 kg/cm<sup>2</sup> gage and then heated at 180°C  
for 30 minutes while passing the hydrogen gas through  
20 the autoclave to conduct hydrogenation. Then, the auto-  
clave was slowly cooled to 20°C, and the precipitated  
crystal was recovered by filtration and dried. The  
resulting trimellitic acid crystal was placed in a  
distilling still and subjected to dehydration and  
25 distillation in the same manner as in Example 1 to  
obtain trimellitic anhydride. The resulting trimellitic  
anhydride had a purity of 99.3 %, a bromine content of

- 1 100 ppm, a TEG color value of 60 and a distillation yield of 97.7 %.

Example 4

- 5 (Direct hydrogenation without solid-liquid separation)

970.5 g of the oxidation product as obtained in Example 1 was charged into an autoclave having a 2-l capacity, provided with a catalyst basket with 1.0 g of 0.5 % Pd/C catalyst, and then the autoclave was  
10 pressurized with a hydrogen gas under a pressure of 15 kg/cm<sup>2</sup> gage, and heated at 120°C for 3 hours while passing the hydrogen gas through the autoclave to conduct hydrogenation. Then, the autoclave was slowly cooled to 20°C, and the precipitated crystal was  
15 recovered by filtration and dried. The resulting trimellitic acid was placed in a distilling still, and subjected to dehydration and distillation in the same manner as in Example 1 to obtain trimellitic anhydride. The resulting trimellitic anhydride had a purity of  
20 99.3 %, a bromine content of 250 ppm, a TEG color value of 90, and a distillation yield of 97.1 %.

Example 5

(Direct hydrogenation without solid-liquid separation)

- 25 970.5 g of the oxidation product as obtained in Example 1 was charged into an autoclave having a 2-l capacity, provided with a catalyst basket with 1.0 g of

1 0.5 % Pd/C catalyst, and then the autoclave was pres-  
surized with a hydrogen gas under a pressure of 68  
kg/cm<sup>2</sup> gage, and heated at 260°C for 60 minutes while  
passing the hydrogen gas through the autoclave to con-  
5 duct hydrogenation. Then, the autoclave was slowly  
cooled to 20°C, and the precipitated crystal was  
recovered by filtration and dried. The resulting tri-  
mellitic acid was placed in a distilling still, and  
subjected to dehydration and distillation in the same  
10 manner as in Example 1 to obtain trimellitic anhydride.  
The resulting trimellitic anhydride had a purity of  
92.1 %, a bromine content of 750 ppm, a TEG color value  
of 250, and a distillation yield of 83.8 %.

15 Example 6

(Solid-liquid separation and hydrogenation)

The oxidation product as obtained in Example 1  
was slowly cooled to 20°C to separate 358 g of precipi-  
tated crude crystal, and the crude crystal was admixed  
20 with 550 g of water in the same manner as in Example 2.

Then, the resulting slurry was charged into  
an autoclave having a 2-l capacity, provided with a  
catalyst basket with 0.5 g of 0.5 % Pd/C catalyst, and  
the autoclave was pressurized with a hydrogen gas under  
25 a pressure of 35 kg/cm<sup>2</sup> gage and then heated at 220°C  
for 30 minutes while passing the hydrogen gas through  
the autoclave to conduct hydrogenation. Then, the



1 autoclave was slowly cooled to 20°C, and the precipi-  
tated crystal was recovered by filtration and dried.  
The resulting trimellitic acid crystal was placed in a  
distilling still and subjected to dehydration and  
5 distillation in the same manner as in Example 1 to  
obtain trimellitic anhydride. The resulting trimellitic  
anhydride had a purity of 94.5 %, a bromine content of  
600 ppm, a TEG color value of 200 and a distillation  
yield of 86.0 %.

10

#### Example 7

(Effect of temperature)

970.5 g of the oxidation product as obtained  
in Example 1 was charged into an autoclave having a 2-l  
15 capacity, provided with a catalyst basket with 2.0 g of  
0.5 % Pd/C catalyst, and then the autoclave was pres-  
surized with a hydrogen gas under a pressure of 20  
kg/cm<sup>2</sup> gage, and heated at 80°C for 3 hours while pass-  
ing the hydrogen gas through the autoclave to conduct  
20 hydrogenation. Then, the autoclave was slowly cooled to  
20°C, and the precipitated crystal was recovered by  
filtration and dried. The resulting trimellitic acid  
was placed in a distilling still, and subjected to  
dehydration and distillation in the same manner as in  
25 Example 1 to obtain trimellitic anhydride. The result-  
ing trimellitic anhydride had a purity of 98.5 %, a bro-  
mine content of 400 ppm, a TEG color value of 140, and

- 1 a distillation yield of 89.9 %.

#### Comparative Example 4

- 5 The oxidation product as obtained in Example 1 was slowly cooled to 20°C to separate 358 g of precipitated crude crystal, and the crude crystal was admixed with 900 g of water and heated at 100°C to obtain a solution.

- 10 Then, 1.5 g of iron powder and 12 g of 35 % hydrochloric acid were added to the solution and kept at 100°C with stirring for 3 hours. Then, the mixture was slowly cooled to 20°C, and the precipitated crystal was recovered by filtration and dried. The resulting trimellitic acid crystal was placed in a distilling still  
15 and subjected to dehydration and distillation in the same manner as in Example 1 to obtain trimellitic anhydride. The resulting trimellitic anhydride had a purity of 96.7 %, a bromine content of 4,800 ppm, a TEG color value of 750 and a distillation yield of 94.2 %.  
20 It was found that the reduction treatment by iron was not effective.

#### Example 8

- 500 g of water and 17.5 g of HBr were charged  
25 into a zirconium autoclave having a 2-l capacity, and then was pressurized with a nitrogen gas under a pressure of 10 kg/cm<sup>2</sup> gage and then heated at 230°C by

1 a heater. Then, 2,4-dimethylbenzaldehyde having a  
purity of at least 99.5 % was supplied to the autoclave  
at a rate of 4.17 g/min. At the same time, air was  
introduced into the autoclave at such a controlled flow  
5 rate as to keep the oxygen concentration of the effluent  
gas from the autoclave at 3 - 4 % by volume. The 2,4-  
dimethylbenzaldehyde was continuously supplied to the  
autoclave for 60 minutes, while the air was continuously  
supplied thereto, even after that, for further 20  
10 minutes to complete the oxidation. After cooling to  
20°C, the oxidation reaction product was taken out.  
The oxidation product had a bromine content of 8,500 ppm  
and had a purity of 94.4 % in terms of trimellitic acid.

962.8 g of the oxidation product containing  
15 333.0 g of trimellitic acid was charged into an auto-  
clave having a 2-l capacity, provided with a catalyst  
basket with 3 g of 0.5 % Pd/C catalyst, and then the  
autoclave was pressurized with a hydrogen gas under a  
pressure of 25 kg/cm<sup>2</sup> gage, and heated at 140°C for  
20 2 hours while injecting the hydrogen gas into the liquid  
phase and passing it through the autoclave to conduct  
hydrogenation. Then, the autoclave was slowly cooled to  
20°C, and the precipitated crystal was recovered by  
filtration and dried. The resulting trimellitic acid  
25 was placed in a distilling still, and heated at 230° -  
240°C under a pressure of 50 - 100 mmHg (absolute) to  
conduct dehydration, and then distilled at 230° - 240°C

1 under a pressure of 4 - 5 mmHg (absolute) to obtain  
trimellitic anhydride. The resulting trimellitic  
anhydride had a purity of 99.1 %, a bromine content of  
240 ppm, a TEG color value of 90, and a distillation  
5 yield of 96.8 %.

#### Example 9

The oxidation product as obtained in Example 8  
was slowly cooled to 20°C to separate 336.4 g of  
10 precipitated crude crystal, and the crude crystal was  
admixed with 550 g of water.

Then, the resulting slurry was charged into  
an autoclave having a 2-l capacity, provided with a  
catalyst basket with 2 g of 0.5 % Pd/C catalyst, and the  
15 autoclave was pressurized with a hydrogen gas under a  
pressure of 15 kg/cm<sup>2</sup> gage and then heated at 165°C for  
1.5 hours while passing the hydrogen gas through the  
autoclave to conduct hydrogenation. Then, the autoclave  
was slowly cooled to 20°C, and the precipitated crystal  
20 was recovered by filtration and dried. The resulting  
trimellitic acid crystal was placed in a distilling  
still and subjected to dehydration and distillation in  
the same manner as in Example 1 to obtain trimellitic  
anhydride. The resulting trimellitic anhydride had a  
25 purity of 99.3 %, a bromine content of 110 ppm, a TEG  
color value of 60, and a distillation yield of 97.3 %.

## CLAIMS :

1. A process for producing an aromatic polycarboxylic acid with high purity, which comprises oxidizing a polyalkyl-substituted aromatic aldehyde or polyalkyl-substituted aromatic carboxylic acid with molecular oxygen in water as a solvent in the presence of bromine ion or bromine ion and heavy metal ion as a catalyst, contacting the oxidation reaction product with molecular hydrogen in the presence of a hydrogenating catalyst at a temperature of 100° to 200°C, and then separating an aromatic polycarboxylic acid from the hydrogenated product.
2. The process according to Claim 1, wherein the polyalkyl-substituted aromatic aldehyde is 2,4-dimethylbenzaldehyde, 3,4-dimethylbenzaldehyde, 2,4,5-trimethylbenzaldehyde or 2,4,6-trimethylbenzaldehyde.
3. The process according to Claim 1, wherein the polyalkyl-substituted aromatic acid is 2,4-dimethylbenzoic acid, 3,4-dimethylbenzoic acid, 2,4,5-trimethylbenzoic acid, or 2,4,6-trimethylbenzoic acid.
4. The process according to Claim 1, wherein the bromine ion is liberated from hydrogen bromide, ammonium bromide, sodium bromide, or alkyl bromide.
5. The process according to Claim 1, wherein the bromine ion is used in an amount of 0.5 - 12% by weight on the basis of the water as the solvent.
6. The process according to Claim 1, wherein the

metal ions of manganese or cerium is used in equivalent amount or less than that to the bromine ion.

7. The process according to Claim 1, wherein the water is used in weight equal to or more than that of the polyalkyl-substituted aromatic aldehyde or the polyalkyl-substituted aromatic acid.

8. The process according to Claim 1, wherein the oxidation is carried out at a reaction temperature of  $180^{\circ} - 280^{\circ}\text{C}$  under a pressure of  $15 - 60 \text{ kg/cm}^2$  gage.

9. The process according to Claim 1, wherein the molecular oxygen is in the form of air.

10. The process according to Claim 1, wherein the hydrogenating catalyst is at least one of noble metals belonging to group 8 of the periodic table.

11. The process according to Claim 11, wherein the noble metals are Pd, Pt, Ru, and Rh.

12. The process according to Claim 1, wherein the hydrogen catalyst is in a simple substance form, an alloy form, a mixture form, or a carrier-supported form.

13. The process according to Claim 13, wherein the carrier is activated carbon in a pellet form.

14. The process according to Claim 1, wherein the hydrogenation is carried out at  $100^{\circ} - 200^{\circ}\text{C}$  under a pressure of  $5 - 30 \text{ kg/cm}^2$  for 0.1 - 8 hours.



European Patent  
Office

# EUROPEAN SEARCH REPORT

0083224  
Application number

EP 82 30 6925

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	GB-A-2 056 979 (MITSUBISHI GAS) *Claims 1-10*	1-9	C 07 C 51/265 C 07 C 51/487 C 07 C 63/307 C 07 C 63/318
X	GB-A-1 152 576 (STANDARD OIL) *Claims 1-4, 6-8, 10, 11; page 1, lines 17-26; page 4, lines 70-90*	1, 10-14	
Y	DE-A-2 743 004 (TEIJIN HERCULES) *Claims 1-3, 5-15*	10-14	
A	GB-A-2 051 039 (MITSUBISHI GAS) *Claim 1*	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 07 C 51/00 C 07 C 63/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24-03-1983	Examiner KLAG M. J.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

